

Synthesis and photophysical characterization of an ionic fluorene derivative for blue light-emitting electrochemical cells



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ABSTRACT

A highly fluorescent an ionic fluorene derivative **1** was synthesized and its photophysical, electrochemical and electroluminescence characteristics were investigated. Deep blue emissions were observed for compound **1** in solid as well as in dilute solutions. The synthesized compound shows high fluorescence quantum yield around 77% indicates that compound **1** can perform its role as efficient ionic emitter in LEC devices. Light-emitting electrochemical cell (LEC) devices were fabricated incorporating compound **1** without (device I) and with (device II) ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆). Devices I and II exhibited blue electroluminescence maximum centered at 455 and 454 nm with CIE coordinates of (0.15, 0.21) and (0.16, 0.22), respectively. Maximum luminance and current efficiency of 1105 cd m⁻² and 0.14 cd A⁻¹ respectively, has achieved for device I while that of device II resulted in 1247 cd m⁻² and 0.14 cd A⁻¹ respectively.

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1. Introduction

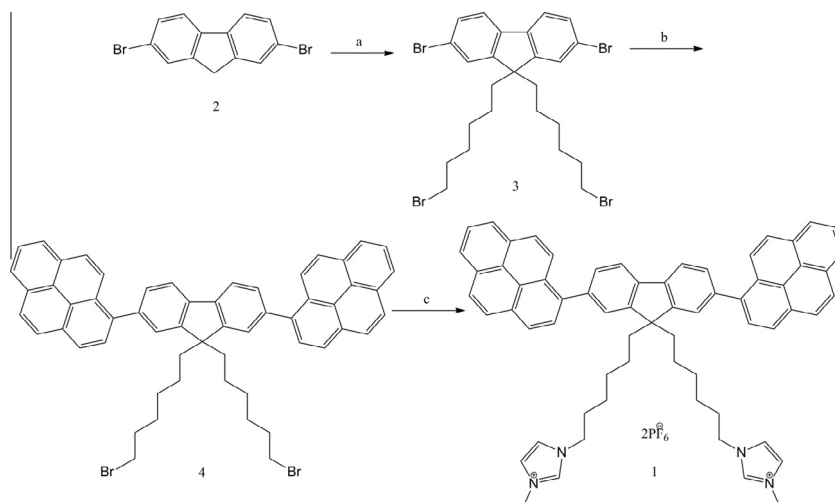
Solution processed light-emitting electrochemical cells (LECs) are anticipated to be the forthcoming generation of flat-panel displays and solid state lighting sources. LEC have great attention due to their high compatibility with low cost and handy fabrication approaches. LECs are conveniently processed from solution and the use of air stable electrodes such as Al, Ag and Au allows non-rigorous encapsulation of the device that operates at low voltages. LECs does not rely on the charge-injection layers due to the presence of mobile ions in the active layer, which makes LECs more impressive compared to the conventional organic light-emitting diodes (OLEDs). Working mechanism of LEC devices involves the transfer of mobile ions present in the active layer which induce electrochemical doping near to the respective electrodes facilitating the injection of holes and electrons and results high power efficiencies in the form of light under the application of an external voltage. In contrast to more stable and highly efficient, sophisticated OLEDs are composed of neutral small molecules processed from thermal evaporation, which makes them more expensive compared to LECs.

In 1995, Pei et al. were reported the first solid state LEC device [1] which consists of a tricomponent blend of a light-emitting polymer, an ion conducting polymer and an inorganic salt. And a year later, Rubner et al. was introduced an alternative using ionic transition metal complexes (iTMCs) as the active material [2]. For the first time, LEC device using iridium-iTMC (Ir-iTMC) were reported in 2004 and produced an intense yellow luminescence with an efficiency of 5% [3]. The Ir-iTMC based LEC devices received great attention in recent years over polymer LECs due to the high photophysical stability, color tunability and phosphorescent nature of the former. An intrinsic ionic character of iTMC has extensive attraction compared to polymer material since iTMC-LEC avoids the use of additional inorganic salts and an ion conducting polymer (polyethylene oxide) as used in polymer LECs. Till to date, Ir-iTMCs have been greatly explored for their performance in LECs and achieved high stabilities, efficiencies and good color purity [4–6].

An extensive number of LEC devices were reported having yellow, orange and red light-emission with remarkable stability and efficient luminescence using cationic iridium complexes [7–18]. However the blue LECs based on iridium complexes are hard-to make because the wide optical energy gaps for blue emitters involve high-energy excitons and exhibited emissions in the bluish-green region [19,20]. Moreover, LECs based on such blue emitting cationic iridium complexes resulted in low efficiency and luminance lifetime [21–24]. Moreover, the high cost and low

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Scheme 1. (a) 1,6-Dibromohexane, TBAB, KOH/H₂O, 75 °C, 15 min; (b) pyrene-1-boronic acid, Pd(PPh₃)₄, K₂CO₃, Toluene/H₂O; (c) 1-methylimidazole, toluene.

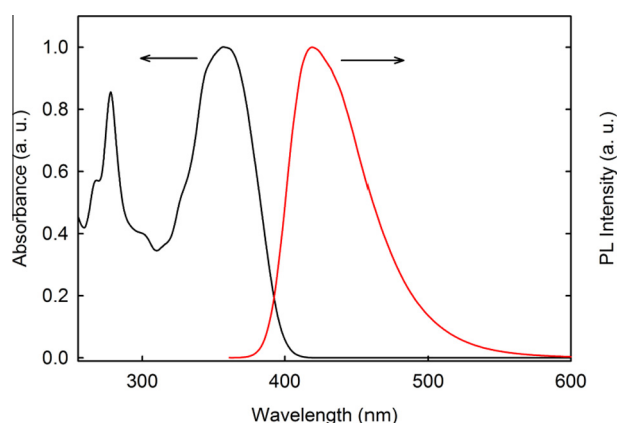


Fig. 1. Normalized absorption and PL spectra of compound 1 in acetonitrile solution (10^{-5} M).

abundance of iridium suppress the large scale production of LEC devices in the future, and hence the development of efficient blue organic emitters for LEC application is highly desirable. In recent years, organic semiconducting materials have attracted much attention due to their excellent performance in optoelectronic devices. By the use of organic semiconductors, efficiency and stability of electroluminescent devices have considerably improved compared to the conventional inorganic materials over a short period of time [25]. In 2013, Tang et al. reported a LEC device using organic non-ionic small molecules (SMs) blended with polyethylene oxide and an inorganic salt as the emitting layer, which exhibited green electroluminescence with peak quantum efficiency of 2.25 cd A^{-1} [26]. Where an ionic organic emitter leads to simpler

thin film architecture were reported for blue LECs with a maximum external quantum efficiency of 1.14% and 1.06% [27,28] respectively, while the cyanine dyes in a host-guest configuration used as active material in LEC device exhibits the luminescence near infra-red region with 0.44% external quantum efficiency [29]. Currently, the low molecular weight compounds, such as an ionic hole-transporter mixed with a neutral polar electron-transporter and a neutral blue-phosphorescent iridium (III) emitter gives an efficient blue LEC with an efficacy of 5 cd A^{-1} [30].

Fluorene including polyfluorenes and its derivatives are used as blue emitters in optoelectronic devices because of their enormous properties, such as large energy gaps, tunable emission color, high luminescence and possible functionalization of the fluorene ring [31–36]. The low molecular weight fluorene analogs have advantages in synthesis, purification and highly pure emission color in comparison with the polyfluorenes [37–39]. In this work, we synthesized an organic ionic small molecule based on a fluorene derivative for their application in electroluminescent devices.

Here, we present a solution processed new blue light-emitting devices exclusively based on an ionic fluorene derivative compound 1 as a light-emitting material without any additional inorganic salt and conducting polymers. LEC devices were fabricated from acetonitrile solution utilizing compound 1 (device I) and the compound 1 containing 10 wt% ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM·PF₆). The fabricated electroluminescent devices exhibits blue electroluminescence for device I and II with Commission Internationale de l'Eclairage (CIE) coordinates of (0.15, 0.21) and (0.16, 0.22), respectively. The maximum luminance of 1105 cd m^{-2} were resulted for device I whereas that of 1247 cd m^{-2} for device II respectively. Our results show that the organic ionic small molecule yields electroluminescence like the ionic phosphorescent molecules without additional components.

Table 1
Photophysical properties of compound 1.

Absorption		Emission λ_{max} (nm)			PLQY ^b	Electrochemical data		
λ_{max} (nm) ^a	Molar absorptivity $\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$	Solution ^a	Solid	Film		HOMO ^c (eV)	LUMO ^d (eV)	E_g^e (eV)
266, 278, 356	5.12, 7.57, 7.98	420	453	454	0.77	−5.64	−2.54	3.10

^a Measured in acetonitrile solution (10^{-5} M) at room temperature.

^b Photoluminescence quantum yields of the compound 1 in acetonitrile solution were measured using 9,10-diphenylanthracene ($\Phi \sim 0.9$) as the standard [45].

^c HOMO energy level were calculated from oxidation onset potential.

^d LUMO energy level were obtained by adding the optical band gap (E_g) to the calculated HOMO energy.

^e The optical band gap (E_g) calculated from the onset of absorption spectrum.

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